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V. G. KHLOPIN

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[A Digest.]

Vitaliy Grigor'evich Khlopin, whose 60th birthday was celebrated on 26 January 1950, was a student of L. A. Chugayev and of the founder of geochemistry, Academician V. I. Vernadskiy. He is a graduate of the universities of Petersburg and Goettingen. Much of his early work was concerned with analytical chemistry, particularly the isolation of compounds of rare metals.

Together with V. V. Lebedev, Khlopin developed a method for the preparation of pure platinum and with B. N. Orelkin and I. I. Chernyayev, a method for the preparation of sodium azide. In 1924, Khlopin and A. I. Lukashuk designed an appliance for the rapid determination of helium together with neon in gas mixtures. In 1932 Khlopin and coworkers developed a method for the rapid determination of the sum of heavy and light noble gases.

In the field of volumetric analysis, Khlopin worked on differential oxidation and reduction as a means of determining separately several cations which are present in the same solution. The application of this method to vanadium, iron, and uranium is of particular interest. He has also devised a method for the rapid determination of quadrivalent uranium by separating it in the form of the complex compound $NH_4UF_5 \cdot 1/2\ H_2O$. In the field of colorimetric analysis, Khlopin developed a method for the determination of traces of iridium in the presence of platinum and also a method for fluorine determination.

Since 1915, Khlopin has actively participated in the work of KEPS (Commission for the Study of Natural Productive Resources). He was called in as a specialist by the Radiological Laboratory of the Academy of Sciences USSR, directed by V. I. Vernadskiy. He has carried out a number of investigations on lithium, rubidium, cesium, and boron the results of which were published by KEPS.

While the work noted above demonstrates Khlopin's versatility as a chemist, it does not reflect accurately his principal field of activity and predominant interest in the chemistry and technology of radioactive substances. Khlopin must be regarded as the creator of the USSR chemistry of radioactive substances and of the technology based on research in that field.

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He established the fundamental relationships governing the behavior of radioactive elements in dilute solutions, developed a general theory of fractional crystallization on which the production of radium from USSR raw material is based, obtained, together with M. A. Pasvik, the first radium preparations produced on an industrial scale in the USSR (according to a process devised by Khlopin), and with V. I. Vernadskiy, created the Radium Institute, a major training school for USSR radiochemists.

Khlopin's work on the behavior of radioactive elements in dilute solutions may be considered revolutionary. It was formerly held that extraction of microcomponents from solution by solid precipitates proceeds according to Fajans' and Paneth's rule to the effect that a radioactive element which is present in solution as a cation is captured by the precipitate to a greater extent accordingly as the solubility of the compound which this cation forms with the anion of the precipitate becomes more limited. This rule was considered valid in cases of both coprecipitation and adsorption. As a result of investigations carried out by Khlopin and coworkers, and also by the German chemist Hahn and his colleagues, genuine and adsorptive coprecipitation could be strictly delimited. Khlopin has shown that the decisive factor which brings about genuine coprecipitation is the existence of isomorphism between the lattice of the macrocomponent (carrier) and the lattice of the microcomponent. He has also defined the conditions under which the microcomponent is distributed between the solution and the crystals of the carrier according to Berthelot-Nernst's law for immiscible liquids, i.e. according to the formula:

$$\frac{\text{Quantity of microcomponent in crystal}}{\text{Volume of crystal}} = K \cdot \frac{\text{Quantity of macrocomponent in solution}}{\text{Volume of solution}}$$

The proof by Khlopin and collaborators of the applicability of this law of distribution to systems consisting of a liquid and a solid phase is of fundamental importance. Once Van't Hoff held that gas laws, including Henry-Dalton's law, are applicable to dilute solid solutions. Later on many physical chemists disputed Van't Hoff's view on the ground that diffusion is absent in isomorphous mixtures, and that consequently an equilibrium distribution of the microcomponent cannot be established. Khlopin and collaborators have shown that multiple recrystallization of particles of the solid phase replaces diffusion, and that by virtue of this recrystallization an equilibrium distribution is achieved. The special formulation of the distribution law for systems consisting of a solid and a liquid phase may very well be called Khlopin's law.

The work of Khlopin and his group has clarified the conditions under which a microcomponent in solution is distributed between the solution and the crystals of the solid phase according to Khlopin's law, as compared with the conditions under which it is distributed according to the logarithmic formula of Doerner-Hoskins. Khlopin's law is applicable only when complete isomorphism exists and, conversely, the fact of its applicability may be regarded as a proof of complete isomorphism. This postulate has enabled Khlopin and others to discover hitherto unknown compounds of divalent and hexavalent polonium and has proven a powerful tool in the field of radioactive elements in general. Using the principle in question, Khlopin was able to discover the existence of a crystalline radon hydrate and to clarify its composition. He was also able to discover several other compounds of noble gases. Khlopin's work on the distribution of microcomponents has proved to be of particular importance in the development of production of radium from USSR raw materials

The work of Khlopin and his school has resulted in a better understanding of the phenomenon of isomorphism. The concept of isomorphism has been considerably expanded as a result of research done in recent years. Classical or genuine isomorphism of the Mitscherlich type is now referred to as isomorphism of the first order, and isomorphisms of the second and third order are assumed to exist in cases where there is no similarity of chemical composition or structure. Isomorphism of an order higher than the first presupposes, on the basis of studies on crystal structure carried out by Grimm and Goldschmidt, that there must be a threshold of the concentration of the microcomponent below which the microcomponent does not enter into the composition of the crystalline phase. The existence of the lower threshold of concentration is due to the fact that whole regions occupied by the main or carrier component must be replaced in crystals the structure of which is based on isomorphism of the latter type, the crystals forming in this case being referred to as anomalous.

Khlopin studied the underlying conditions by using radioactive indicators and established that capture of microcomponents in the form of constituents of anomalous mixed crystals is much more widespread than had been assumed. In other words, the phenomenon is of great practical importance for the isolation of microcomponents.

In addition to carrying out extensive investigations in the fields of radioactive elements and general chemistry, Khlopin has cooperated with Academicians V. I. Vernadskiy and A. E. Fersman in research on the geochemistry of radioactive elements. Systematic investigations of the occurrence of radium and radioactive isotopes in water of oil wells and brines of a certain type found at a great depth in oil fields were carried out under his supervision. Khlopin's collaborators clarified the mechanism of formation of natural radium-bearing waters. Khlopin and collaborators have worked on the evolution of helium from minerals and rock occurrences. The state in which helium occurs is not always the same and the energy of activation necessary for the separation of bound helium differs accordingly. While the helium method can be used for determining the age of minerals, it does not work in cases where the age of a rock stratum or species has to be determined.

Being a pioneer in university instruction in radioactivity and radiochemistry (at the Leningrad University), Khlopin is widely active in the organization of instruction in that field elesewhere. He also acts as a consultant at numerous enterprises and organizations concerned with the production and utilization of radium and noble gases. Besides being a permanent director of the Radium Institute since 1938, Khlopin during World War II directed the activities of the Department of Chemical Sciences of the Academy of Sciences USSR. As acting Academician-Secretary he on numerous occasions acted as Vice-President of the Academy of Sciences USSR. He also was acting chairman of the Commission for Mobilization of Resources of the Volga and Kama Regions.

Khlopin has been honored by many government awards and prizes. By invitation of the Leningrad section of the Mendeleyev Society, he gave in 1941 the first Mendeleyev lecture on the subject "Transmutation of Elements and the Periodic Law."

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